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(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
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Coating layer

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Coating layer

Polymer coated drawn and wall ironed (DWI) beer and beverage cans are gaining more and more interest. The advantage of such a can is that the can maker does not have to apply an in-can lacquer. This not only avoids the use of volatile components but also simplifies the production chain and makes the process economically viable at smaller outputs.

Mineral water can be considered to be amongst the most critical filling goods for a steel beverage can. Besides flavour retention, corrosion resistance of DWI polymer coated beverage cans in combination with mineral water has proven to be critical. From the plastic bottle industry, it is known that polyethylene terephthalate (PET) can be used for mineral water packing. These bottles generally consist of highly oriented and crystallized PET; special grades of PET are available in order to ensure sufficient flavour retention.

On translating this technology to steel beverage cans, a number of performance issues are encountered. Firstly, standard PET grades do not show sufficient adhesion to steel after wall ironing of the PET coated steel cup. This issue can be resolved by using a thin layer of specially modified PET grades (e.g. iso-phthalic acid (IPA) or cyclohexane dimethanol (CHDM) modifications), optionally in combination (blend or copolymerisation) with standard PET.

Secondly, beverage cans filled made from thin metal always show a limited amount of dome growth caused by the pressure volume behaviour under influence of temperature variations. In the case of PET coated beverage cans, this results in cracking of the coating and subsequent corrosion in the bottom channel on prolonged testing. This, in turn, results in unacceptably high levels of iron pick-up in the filling good. Yet another difference of a polymer coated beverage can (compared to a tinplate can) is the seam. After filling, the can is closed whereby the lid is normally attached to the neck of a flanged can by a seaming operation. The polymer coated, drawn and wall ironed necked material, is again plastically deformed with the contents in the can. This leads to coating stresses that cannot be relieved by heat treatments. This in turn may lead to brittle failure of the coating.

Another issue is the dent resistance of the can. US laid-open patents 6,136,395 and 5,653,357 (Toyo Seikan Kaisha, Ltd.) describe that standard PET or polyethylene isophthalic acid (PET/I) modified PET coatings are prone to cracking and permeation on impact and/or denting.

The aforementioned issues obviously imply compromised shelf life of the can. All have in common that the PET coated beverage cans are prone to cracking of the coating and subsequent corrosion in the bottom channel, body hook radius and/or dented locations on prolonged testing.

In the present invention, a new 3-layer coating on a metal (preferably steel) substrate is described, the substrate/coating system being able to pack mineral water. The polymer coated steel shows excellent can-making performance. Additionally, the resulting can shows good corrosion resistance and the coating shows excellent stress-crack resistance and adhesion to the substrate. The latter enables (thermal) decoration and necking (up to 202 necks) of the decorated can.

In initial attempts to pack mineral water in PET coated tin-free steel (TFS) beverage cans, a PET coating specification was used consisting of an adhesion layer containing modified (either by IPA or CHDM) PET and a top layer consisting of a standard (water bottle grade) PET, the typical total thickness of the coating being 30 microns. The latter was observed to be the required thickness in order to obtain pore-free cans after cupping, wall-ironing (>50% total wall reduction) and necking. Can making was performed using a cupping, redrawing and wall-ironing process. After filling the cans with mineral water and closing, the cans were stored at elevated temperature. For some cans, purposely dome growth was initiated. After 1 and 3 months, they were examined with respect to iron pick-up and corrosion. Using this standard specification, severe corrosion as well as unacceptably high levels of iron-pick-up was observed. Corrosion was found mainly in the bottom channel and the body hook radius of the can. This was attributed

to dome growth and the seaming operation followed by subsequent stress cracking of the coating. In order to circumvent this, a specification was made using the aforementioned types of modified PET adhesion layers and PET/PBT blend top-layer, coated onto steel. Surprisingly, already at PBT levels as low as 20%, stress-cracking resulting from dome growth after filling and storing of cans vanished, resulting into pore-free and corrosion-free cans after prolonged storage (>3 months) at elevated temperatures. A main drawback of the system was, however, that can making performance of the described specification was greatly compromised in long can making runs. This was attributed to the rather low glass transition temperature of PBT (~30 °C). Already after 50 cans, the body maker and the wall ironing punch started to warm-up giving rise to sticking of the cans to the wall ironing punch, making it impossible to produce cans in larger quantities. Clearly, this is unacceptable for continuous can making in a production environment.

The invention describes a coating system where the aforementioned issues are resolved. The following types of 3-layer coatings were produced:

Adhesion layer:

Modified PET system (e.g. by IPA or CHDM or combinations thereof) obtained either by blending or copolymerisation with PET, showing excellent adhesion to steel both prior to and after can making and sterilisation/pasteurisation.

Main layer:

Blend or copolymer system comprising PET and PBT showing excellent resistance towards stress-cracking.

Top layer:

PET or modified PET system (either by copolymerisation and/or blending) having sufficient not-stick properties at elevated temperatures in order to allow DWI can making at high speeds and in large runs.

In the preferred embodiment, the adhesion layer consists of approximately 70% PETG (PET modified by CHDM co-monomer) and approximately 30% of bottle grade PET. The thickness of this layer is approximately 6 microns. The main layer consists of a blend of PET and PBT in a typical ratio of 1 to 1. The typical thickness of this layer is approximately 18 microns. The top layer consists of a standard PET bottle grade having a standard glass transition temperature and melting point. The typical thickness of this layer is approximately 6 microns.

The coating can be easily prepared by co-extrusion, using standard extruders and a feed-block/ die set-up. Alternatively, the coating can be applied as subsequent layers. Coating onto the metal substrate (preferably tin-free steel) can be accomplished either by direct co-extrusion or by first preparing a film (and optionally stretching it) and subsequently coating it onto the substrate.

It should be noted that the use of the present invention is not limited to packing mineral water. In trials with cola, it was shown that iron pick-up can be greatly decreased by using the coating of the present invention compared to a standard PET coating.

Example 1 (preferred embodiment of the invention)

The following coating recipe was co-extruded: Adhesion layer (6 microns): 70% PETG (containing 37% CHDM co-monomer) blended with 30% standard PET (water bottle grade). Main layer (18 microns): 50% standard PET blended with 50% PBT. Top layer (6 microns): 100% standard PET. The co-extrudate was coated onto tin-free steel (0.19 mm, T57 BA) by direct extrusion, the total coating thickness being 30 microns. The reverse side of the strip was simultaneously extrusion coated with a standard 20 micron PET specification. After coating, the material was post-heated at 270 °C and rapidly quenched with water at room temperature.

The resulting polymer coated strip was fed to a DWI line and beverage cans were produced (the 3-layer coating of the invention being on the inside of the can). Production ran smoothly and no can making issues were observed. A total of ~300 cans were made, the average E470 porosity value being 0.70 mA.

The resulting cans were filled with mineral water, closed and pack tested at 35 °C for 3 months. For a number of cans, purposely dome growth was initiated. After opening and emptying the cans, they were inspected with respect to corrosion. Additionally, the iron pick-up was determined. No corrosion in the bottom channel was observed, both for can with and without dome growth. Furthermore, the iron pick-up turned out to be significantly lower compared to the standard PET reference (example 3) in the case of dome growth. The results with respect to can making, corrosion and iron pick-up are presented in table 1.

Table 1: Mineral water: Preferred embodiment, example 1.

Can	Bottom growth	Length corrosion bottom channel (mm)	Fe content (mg/l)	Can making performance
1.	Yes	0	1,74	Excellent
2.	Yes	0	0,78	
3.	Yes	0	0,35	
4.	Yes	0	1,12	
5.	Yes	0	0,63	
6.	Yes	0	0,37	
7.	Yes	0	0,71	
8.	No	0	0,15	
9.	No	0	0,12	
10.	No	0	0,12	

Comparative example 2

Identical to example 1 but in this case a 2-layer system was made with the following specification: Adhesion layer (6 microns): 70% PETG blended with 30% standard PET. Main layer (24 microns): 50% PBT blended with 50% PET.

On running (already after ~25 cans), can making resulted in stick on punch of the cans after wall ironing, greatly compromising the line continuity. In a discontinuous set-up, ~250 cans were produced, the average E470 porosity value being 0.70 mA.

After pack testing the cans with mineral water as described in example 1, corrosion in the bottom channel was determined. Corrosion was measured by determining the arc-length of the corroded area in the bottom channel. In the case where the complete bottom channel was covered with corrosion products, the reported length would be 157 mm, being equivalent to the circumference.

The results with respect to can making, corrosion and iron pick-up are presented in table 2.

Table 3: Mineral water: Comparative example 2.

Can	Bottom growth	Length corrosion bottom channel (mm)	Fe content (mg/l)	Can making performance
1.	Yes	100	0.52	Poor
2.	Yes	5	nd	
3.	Yes	60	1,48	
4.	No	0	0,04	
5.	No	0	nd	
6.	No	0	nd	
7.	No	0	nd	
8.	No	0	nd	
9.	No	0	nd	
10.	No	0	nd	

Comparative example 3 (standard PET reference)

Identical to example 1 but in this case a 2-layer system was made with the following specification: Adhesion layer (6 microns): 70% PETG blended with 30% standard PET. Main layer (24 microns): 100% PET.

Can making ran excellent, also on prolonged running. A total of 1000 cans were made, the average E470 porosity value being 0.70 mA. After pack testing with mineral water, however, severe corrosion in the bottom channel was observed (measured as described in example 2) as well as unacceptably high levels of iron pick-up. The results with respect to can making, corrosion and iron pick-up are presented in table 3.

Table 3: Mineral water: standard PET reference, comparative example 3.

Can	Bottom growth	Length corrosion bottom channel (mm)	Fe content (mg/l)	Can making performance
1.	Yes	157	36,5	Excellent
2.	Yes	157	32,8	
3.	Yes	157	32,7	
4.	Yes	157	27,4	
5.	Yes	157	34,8	
6.	Yes	157	35,0	
7.	Yes	157	33,5	
8.	Yes	157	14,1	
9.	No	0	0,08	
10.	No	0	0,08	
11.	No	0	0,18	
12.	No	0	0,06	
13.	No	0	0,04	
14.	No	0	0,07	
15.	No	0	0,03	
16.	No	0	0,05	
17.	No	0	nd	
18.	No	0	nd	
19.	No	0	nd	
20.	No	0	nd	
21.	No	0	nd	
22.	No	0	nd	
23.	No	0	nd	
24.	No	0	nd	
25.	No	0	nd	
26.	No	0	nd	
27.	No	0	nd	
28.	No	0	nd	

The results of examples 1-3 are summarized in table 1.

Example	Adhesion layer	Main layer	Top layer	Corrosion resistance	Can-making performance
1.	6 μ 70% PETG/30% PET	18 μ 50% PBT/50% PET	6 μ 100% PET	++	++
2.	6 μ 70% PETG/30% PET	24 μ 50% PBT/50% PET	None	++	-
3.	6 μ 70% PETG/30% PET	24 μ 100% PET	None	--	++

Claim

1. A coating comprising:

- An adhesion layer comprising PET, modified PET and/or combinations thereof, by blending and/or copolymerisation, being able to accomplish sufficient adhesion to metal, preferably steel, in beverage can application; and
- A main layer comprising PET, PBT and/or combinations thereof, by blending and/or copolymerisation; and
- A top layer comprising standard PET, having a sufficiently high melting point and glass transition temperature in order to avoid tacking (softening) at low temperatures (such as below 100 °C).

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